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Theoretical Estimates of Redox Potentials for Group 6 Elements, Including Element 106, Seaborgium, in Acid Solutions

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Standard reduction potentials for group 6 elements, including element 106 (Sg), in acid solutions have been estimated on the basis of ionization potentials calculated using the multiconfiguration Dirac−Fock method. The stability of the 6+ oxidation state is shown to increase within group 6, while that of the 5+, 4+, and 3+ states is shown to decrease. No extra stability of the 4+ oxidation state of Sg can be inferred. Thus, no deviation from the Mendeleev-type periodicity is found for group 6 elements.

I. Introduction

The question about stable oxidation states of an element is one of the most important since many other physical and chemical properties depend on the oxidation state. No less important is the question about the relative stability of the oxidation states, or standard electrode potentials. This is particularly valid for the transactinides, the 6d elements, where relativistic effects on the valence electron shells are very strong.

It is known that the stability of the maximum oxidation state increases within transition element groups.[1] A possible deviation from this trend of elements 103 and heavier was expected because of the relativistic stabilization of the $7s^2$ and $7p_{1/2}$ electrons. Thus, the 1+ state was foreseen for element 103, Lr; the 1+ and 2+ states for element 104, Rf; the 3+ state for element 105, Db; and the 4+ state for element 106, Sg.[2−4]

The 4+ state for Sg as the most stable was proposed by Penneman and Mann[4] using Jørgensen's equation[5] based on a Born−Haber cycle where atomic ionization potentials (IP) were obtained via the Dirac−Fock (DF) calculations[6] and sublimation enthalpies of metals were estimated by simple extrapolations. The 6+ oxidation state, in turn, was suggested as the most stable by Cunningham[7] using extrapolations within the periodic table. The results are summarized in the review of Fricke.[8] We note here that Jørgensen's formula was designed only for hydrated cations and does not account for the effects of complex ion formation. Nevertheless, it is known that elements of the 4d and 5d series in high oxidation states do not form simple hydrated ions in solutions but rather complex ions. The effect of the complex formation should be even more pronounced for the 6d elements having smaller excitation energies between the valence orbitals. Therefore, it is not the simple Sg^{4+} ion, but a complex one (with Sg in a higher oxidation state) that will be predominant in aqueous acid solutions whose stability and redox potentials corresponding to oxidation−reduction processes should be evaluated.

The question about stability of the oxidation states of elements Rf, Db, and Sg has further been investigated by us on the basis of multiconfiguration Dirac−Fock (MCDF) atomic calculations[9,10] and molecular Dirac−Slater discrete variational (DS-DV) ones.[11−13] As a result, complete schemes of standard potentials have been derived for Rf and Db and some potentials, such as $E°$ ($SgCl_6/SgCl_5$) and $E°$ (SgO_4^{2-}/SgO_4^{3-}), for Sg. These investigations[9−13] have shown Rf and Db to be the most stable in the 4+ and 5+ states, respectively, in accordance with the known trend to an increase in the stability of the maximum oxidation state in those groups. No extra stability of the 3+ oxidation state has been predicted for Db.[10]

Our recent estimates of redox potentials for elements Rf through Sg have also shown the stability of the maximum oxidation state to decrease within the 6d series, so that beyond element 106 lower oxidation states will obviously be preferred in aqueous solutions.[10−13] A correlation between energies of charge transfer electronic transitions in the $RfCl_4$, $DbCl_5$, and $SgCl_6$ complexes calculated using the DS-DV method and related reduction potentials $E°$ (M^{IV}/M^{III}), $E°$ (M^{V}/M^{IV}), and $E°$ (M^{VI}/M^{V}), respectively, has given $E°$ ($RfCl_4/RfCl_3$) $= -1.5$ V, $E°$ ($DbCl_5/DbCl_4$) $= -1.0$, and $E°$ ($SgCl_6/SgCl_5$) $= -0.93$ V.[12] These values are indicative of a decrease in the stability of the maximum oxidation state in the row $RfCl_4$, $DbCl_5$, and $SgCl_6$. A similar correlation for the group 6 MO_4^{2-} (M = Mo, W, and Sg) complexes has given $E°$ (SgO_4^{2-}/SgO_4^{3-}) $= -1.6$ V.[11] This value shows a slight increase in the stability of the 6+ oxidation state of Sg in comparison with those states of Mo and W.

To complete the scheme of the redox potentials for Sg and to solve the question about stability of the 4+ oxidation state, a complete set of redox reactions for group 6 elements in aqueous acid solutions is considered in the present publication. Estimates of redox potentials have been made on the basis of results of calculations[14] of IPs of atoms and ions of Cr, Mo, W, and Sg using the multiconfiguration Dirac−Fock (MCDF)

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method.[15] In section II, the used approach is presented. Results and their discussion are given in sections III and IV.

II. Method of Estimates

The method of estimates has been described in our previous publication devoted to the prediction of redox potentials for Db.[10] We repeat here the main features of this approach.

The reduction reaction for an element M in an oxidation state $z+n$ when transformed into an ion with a charge $z+$ is written in the following way

$$M^{z+n} + ne \leftrightarrow M^{z+} \tag{1}$$

The change in the free energy ΔG of reaction 1 is

$$\Delta G = -nFE \tag{2}$$

where F is the Faraday number, E is the reduction potential, and n is the number of transferred electrons. A potential is referred to as an $E°$ value if all dissolved substances are at an activity of 1 molal.

With respect to the standard hydrogen electrode, the potential is related to the free energy change of the reaction

$$M^{z+n}{}_{aq} + 1/2nH_2(g) \leftrightarrow M^{z+}{}_{aq} + nH^+ \tag{3}$$

By neglecting the entropy change, which is supposed to be small, the standard reduction potential for reaction 3 can be expressed in terms of a Born−Haber cycle

$$E°(M^{z+n}/M^{z+}) = 1/n[(IP(0/z+n) - IP(0/z+)) + (\Delta H_{hydr}(M^{z+}) - \Delta H_{hydr}(M^{z+n})) - (1/2nDH_2 + nIP_H - n\Delta H_{hydr}(H^+))] \tag{4}$$

where IP($0/z+n$) and IP($0/z+$) are multiple IPs corresponding to the transition from the neutral to the $z+n$ and $z+$ ionized states, respectively; ΔH_{hydr} is the hydration energy

$$\Delta H_{hydr}(M^{z+}) = A(z)/\epsilon[r_{M(z+)} + r_{x(z)}] \tag{5}$$

where ϵ is the dielectric constant of water, $r_{M(z+)}$ is the ionic radius of the metal ion, $r_{x(z)}$ is a radius parameter to be added to the crystal radius, and DH_2 is the dissociation energy of H_2.

By taking into account the quantities for H_2, eq 4 can be rewritten in the following way

$$E°(M^{z+n}/M^{z+}) = 1/n[\Delta IP(z+n/z+) + \Delta H_{hydr}(M^{z+}/M^{z+n}) - 4.66]V \tag{6}$$

Thus, $E°$ is defined by differences in the IP and hydration energy terms. (One should note here that ΔIP must correspond to a transition from the lowest electronic state of the $z+x$ charge state to the lowest electronic state of the $z+$ charge state, so that possible changes in the electronic configurations are included.)

By using eq 6, reduction potentials for simple hydrated cations can be calculated provided the hydration energy change term is estimated. The latter is known to be a source of uncertainty. Equation 6 does not, however, account for the complex formation which takes place in aqueous solutions of transition elements in high oxidation states. Therefore, the idea suggested by us[10,16] is not to calculate $E°$ using eq 6, but to use a linear correlation between $E°$ and ΔIP. The validity of this approach is seen from the following.

TABLE 1: Standard Free Energies of Formation, $\Delta G_f°$ (in eV), Ionization Potentials, IP(0/6+) (in eV), and Standard Reduction Potentials $E°$ (in V) for M^{VI}/M Couples of Group 6 Compounds

property	Cr	Mo	W	Sg
IP(0/6+), eV[a]	263.48	214.06	203.61	192.57
$\Delta G_f°(MO_3)$[b]	−310.97[d]	−159.65	−182.60	−185.98[f]
$\Delta G_f°(H_2MO_4)$[b]	−310.97[d]	−218.0[e]	−239.0[e]	−242.67[f]
$E°(MO_3, H^+/M)$[c]	0.31[d]	0.075	−0.091	(−0.12)[f]
$E°(H_2MO_4, H^+/M)$[c]	0.31[d]	0.06	−0.08	(−0.12)[f]
$E°(M^{VI}, H^+/M)$[c]	0.31[d]	0.082[g]	−0.06[h]	(−0.09)[f]

[a] Reference 14. [b] Reference 21. [c] Reference 18. [d] For $Cr_2O_7{}^{2-}$. [e] Reference 22. [f] This work. [g] For the ($H_3Mo_7O_{24}{}^{3-}$, H^+/Mo) couple. [h] For the ($H_3W_6O_{21}{}^{4-}$, H^+/W) couple.

It was shown[10,16] that for a series of homologous compounds, a change in the hydration energy $\Delta H_{hydr}(M^{z+}/M^{z+n})$, where ΔH_{hydr} is expressed by eq 5, is a smooth function of atomic number or even a constant value, so that $E°$ (M^{z+n}/M^{z+}) linearly correlates with ΔIP($z+n/z+$). Examples of such correlations can be found for the case of the lanthanide and actinide series[16] and for group 5 elements including Db.[10] Our recent MCDF calculations[14] of the electronic structure of the group 6 elements, Cr, Mo, W and Sg, and their positive ions have analogously shown that differences in ionic radii (IR) for the two, $z+n$ and $z+$, states and, hence, $\Delta H_{hydr}(M^{z+}/M^{z+n})$ are also very similar, so that the correlation expressed by eq 6 is valid.

The same can be applied to complexes of Cr, Mo, W, and Sg. There, the hydration energy term should only include the ionic radius of the entire complex, with ΔH_{hydr} for analogous complexes of M^{z+n} and M^{z+} of group 6 elements being also equal to the difference in the IR of central metals, and, hence, being also almost a constant value for a series of homologous compounds. The differences in the additional dissociation energy terms of a Born−Haber cycle for compounds/complexes of the element in the $z+n$ and $z+$ oxidation states will be presumably also similar for homologues in the same chemical group, so that the linear correlation expressed by eq 6 is still valid.

For a half reaction (where $z = n$)

$$M^{z+} + ne \Leftrightarrow M(s) \tag{7}$$

the reduction potential $E°(M^{z+}/M)$ will be approximately given by

$$E°(M^{z+}/M) = 1/n[S + IP(0/z+) - \Delta H_{hydr}(M^{z+}) - 4.66]V \tag{8}$$

where S is the heat of sublimation. Similar to eq 6, eq 8 is to be used as a basis for a linear correlation between $E°$ and IP. The heat of sublimation for Cr, Mo, W, and Sg is 4.076, 6.799, 8.80, and 8.369 (or 8.933) eV,[17] respectively, while the values of IP(0/6+) are above 200 eV (see Table 1). Thus, the IPs are sufficient in magnitude to establish the trend in $E°(M^{VI}/M)$ and the correlation between these quantities.

Values of the IPs have been obtained as a result of the MCDF calculations[14] of the electronic structure of Cr, Mo, W, and Sg atoms and ions. Transitions between different states include changes in electronic configurations. Thus, for Sg: IP(0/1+) $= E(d^4s^2) - E(d^3s^2)$; IP(1+/2+) $= E(d^3s^2) - E(d^3s^1)$; IP(2+/3+) $= E(d^3s^1) - E(d^3)$; IP(3+/4+) $= E(d^3) - E(d^2)$; IP(4+/5+) $= E(d^2) - E(d^1)$; and IP(5+/6+) $= E(d^1) - E$(core). The calculated IPs have been extrapolated and normalized to experimentally known values (see ref 14). Since some of the experimental IPs, e.g., IP(4+/3+) = 46.4 eV for Mo, have obviously been measured with insufficient accuracy, a new set of the IP values called "empirical" has been used for the present correlations. Experimental values of $E°$ have been taken from ref 18, a most complete and revised version. Some earlier data of Latimer[19]and of others[20] are also discussed.

III. Redox Reactions of Cr, Mo, W, and Sg in Aqueous Acid Solutions

A. Oxidation states and species of Cr, Mo, and W. The group 6 elements have six valence electrons. In the gas phase, the electronic configurations are Cr($3d^5 4s^1$), Mo($4d^5 5s^1$), W($5d^4 6s^2$), and Sg($6d^4 7s^2$). In solutions, oxidation states of Cr, Mo, and W range from 2+ to 6+.[1,19,20]

In compounds, Cr has the most common oxidation states 2+, 3+, and 6+. The most stable and important oxidation state is 3+. For Mo and W, the 6+ oxidation state is the most important. The data for Cr, Mo, and W show that the stability of the 6+ oxidation state increases within the group, while that of the 4+ and 3+ states decrease. Whether Sg is in line with this trend will be seen from the following.

B. Reduction Reactions $M^{VI} \rightarrow M$. Compounds of Cr^{VI} are strong oxidizing agents. CrO_3 is known, but in acid solutions, $Cr_2O_7^{2-}$ is formed.

The most important state of Mo is 6+ and the chemistry of this state is largely that of the oxide, MoO_3. The solid acid is H_2MoO_4 which is polymeric. Aqueous phase species are polymeric $H_3Mo_7O_{24}^{3-}$ ions.

WO_3 is well known. The solid acid is H_2WO_4 though it is doubtless one of the polyforms. An aqueous form of W^{VI} is the polymeric ion $H_2W_6O_{21}^{4-}$. In aqueous solutions, Mo^{VI} and W^{VI} cannot be reduced below M^{3+}.

To calculate $E°(MO_3/M)$ (M = Mo and W), the following reduction reaction was used[18−20]

$$MO_3(c) + 6H^+ + 6e \Leftrightarrow M(c) + 3H_2O \qquad (9)$$

Since CrO_3 is not stable in solutions and no redox potential $E°(CrO_3/Cr)$ is known, $Cr_2O_7^{2-}$ will be used instead in further correlations.

Redox potentials for reaction 9 for Mo and W have been calculated[18] from the free energies of formation[21] (Table 1) using the thermodynamic equation

$$E^o = \frac{1}{6}\,\frac{3\Delta G_f°(H_2O) - \Delta G_f°(MO_3)}{F} \qquad (10)$$

The $E°$ values are shown in Table 1. By analogy with Mo and W, Sg is also supposed to form SgO_3. $E°(SgO_3/Sg)$ has been obtained by a linear correlation (eq 8) between $E°$ ($Cr_2O_7^{2-}$/Cr), $E°(MO_3/M)$, where M = Mo and W, and IP(0/6) (Figure 1). (This correlation and all further going are least-squares fits to the data.) The relatively loose correlation can be explained by a different form of Cr^{VI} than those of Mo and W. The obtained value of $E°(SgO_3/Sg) = -0.12$ V.

For the $E°(H_2MO_4/M)$ potentials, the following reaction was used[18]

$$H_2MO_4(c) + 6H^+ + 6e \Leftrightarrow M(c) + 4H_2O \qquad (11)$$

The corresponding values of $E°(H_2MO_4/M)$ for Mo and W are shown in Table 1. The same value of $E°(H_2SgO_4/Sg) = -0.12$ V is obtained by a correlation between $E°(H_2MO_4/M)$ and IP(0/6+) which is very similar to the one shown in Figure 1.

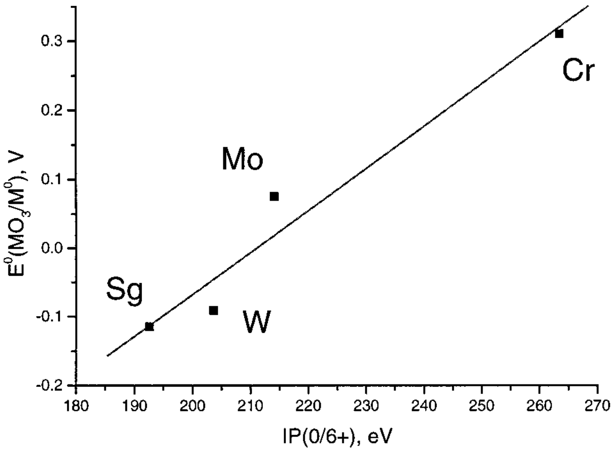

Figure 1. Correlation between IP(0/6+) and the standard potentials, $E°(Cr_2O_7^{2-}/Cr)$ and $E°(MO_3/M)$, where M = Mo and W, (Table 1). The obtained $E°(SgO_3/Sg) = -0.12$ V.

TABLE 2: Standard Free Energies of Formation, $\Delta G_f°$ (in eV), Ionization Potentials, IP(5+/6+) (in eV), and Standard Reduction Potentials $E°$ (in V) for the M^{VI}/M^V Couple of Group 6 Compounds

property	Cr	Mo	W	Sg
IP(5+/6+), eV[a]	90.68	68.79	64.68	59.24
$\Delta G_f°(M_2O_5)$[d]		−294.8	−306.9[b]	−316.6
$E°(MO_3, H^+/M_2O_5)$[c]	(1.3)[e]	(0.7)	(−0.034)[f]	(−0.046)[f]
$E°(H_2MO_4, H^+/M_2O_5)$[c]	(1.3)[e]	(0.6)	(0 ± 0.01)[f]	(−0.05)[f]
$E°(M^{VI}, H^+/M^V)$[c]	(1.1)[g]	(0.6)[h]	(−0.04)[f,i]	(−0.05)[f]

[a] Reference 14. [b] Reference 19. [c] Reference 18. [d] Calculated in this work using reaction 13. [e] For the ($Cr_2O_7^{2-}$, H^+/Cr_2O_5) couple. [f] This work. [g] For the ($Cr_2O_7^{2-}$, H^+/H_3CrO_4) couple. [h] For the ($H_3Mo_7O_{24}^{3-}$, $H^+/Mo_2O_4^{2+}$) couple. [i] For the ($H_2W_6O_{21}^{4-}$, H^+/W^V) couple.

A similar linear correlation between $E°(M^{VI}/M)$ and IP(0/6+) for aqueous species of Cr, Mo, W, and Sg has resulted in $E°(Sg^{VI}/Sg) = -0.09$ V (Table 1). For this correlation, $E°$ has been taken for polymeric forms of Cr, Mo, and W, though Sg obtained in a "one-atom-at-a-time" amount is a monomeric species denoted as Sg^{VI}.

For aqueous HCl solutions, there are very few data[19,20] on redox potentials of Mo and W with most of them being inconsistent, so that they cannot be used for the present systematic study.

Thus, in accordance with our earlier predictions,[12,13] estimated reduction potentials $E°(Sg^{VI}/Sg)$ (Table 1) are indicative of an increase in the stability of the 6+ oxidation state within group 6: Cr < Mo < W < Sg.

By using $E°(SgO_3/Sg)$, the free energy of formation of SgO_3 = −185.98 kcal/mol has been calculated using eq 10 (see Table 1). In a similar way, $\Delta G_f°(H_2SgO_4) = -242.67$ kcal/mol has been obtained using reaction 11. Thus, the stability of MO_3, H_2MO_4 and of the other species of M^{VI} increases within the group from Mo to Sg.

C. Reduction Reaction $M^{VI} \rightarrow M^V$. The oxidation state 5+ is not important for Cr. In acid solution, CrO_4^{3-} disproportionates to CrO_4^{2-} and Cr^{3+}. Redox potentials Cr^{VI}/Cr^V (also for the Cr_2O_5 species) have been estimated[18] using thermodynamic data (Table 2).

Mo^V species are relatively stable. The Mo^V oxide is known as Mo_2O_5. Aqueous Mo^V species in acid solutions are derivatives of the MoO_2^+ ion. At 1 M H^+, the reduction of molybdic acid proceeds in the following way

$$H_2MoO_4(aq) + 2H^+ + e \Leftrightarrow MoO_2^+ + 2H_2O \qquad (12)$$

In very dilute aqueous solutions, MoO_2^+ is dimerized to $Mo_2O_4^{2+}$.

W_2O_5 is mentioned.[19] The structure of soluble W^{V} in very dilute solutions is not known, though with an excess of acid, complexes such as $W(OH)Cl_5^-$ can be formed. Potentials M^{VI}/M^{V} for crystalline compounds and for aqueous species in noncomplexing media for Mo and W have been estimated (Table 2) from thermodynamic data.[18]

In hydrochloric acid solutions, $E°(Mo^{VI}/Mo^{V})$ and $E°(W^{VI}/W^{V})$ have been measured[19,20] at some HCl concentrations. These values are lower than the corresponding ones in the noncomplexing media: e.g., $E°(Mo^{VI}/Mo^{V}) = 0.53$ V[19,20] in 2 N HCl, while $E°(Mo_7O_{24}^{6-}/Mo_2O_4^{2+}) = 0.6$ V. These data are, however, not consistent, so that they cannot be used in correlations using the present approach. The knowledge of them is, nevertheless, valuable to get a feeling of a change of a potential in going from very dilute to more concentrated acid solutions.

For systematic estimates of the reduction potentials for the couple M^{VI}/M^{V}, the following reactions were used

$$2MO_3(c) + 2H^+ + 2e \Leftrightarrow M_2O_5(c) + H_2O \tag{13}$$

$$2H_2MO_4(c) + 2H^+ + 2e \Leftrightarrow M_2O_5(c) + 3H_2O \tag{14}$$

The main problem here is the absence of reliable values of $E°(W^{VI}/W^{V})$ and $E°(W^{V}/W^{IV})$. This will make the prediction of $E°(Sg^{VI}/Sg^{V})$ very approximate. Thus, Latimer[19] gives $E°(WO_3/W_2O_5) = -0.03$ V and $E°(W_2O_5/WO_2) = -0.04$ V, which make potential $E°(WO_3/WO_2) = -0.03$ V. These values were calculated from the old data[19] of free energies of formation. In ref 20, $E°(WO_3/W_2O_5) = -0.029$ V and $E°(W_2O_5/WO_2) = -0.031$ V, which make potential $E°(WO_3/WO_2) = -0.03$ V. Revised data of Bratsch[18] give $E°(WO_3/WO_2) = 0.036$ V on the basis of more recent values of $\Delta G_f°(WO_3)$ and $\Delta G_f°(WO_2)$.[21] To our knowledge, there are no new data on $\Delta G_f°(W_2O_5)$.

Thus, we can recalculate $E°(WO_3/W_2O_5)$ (reaction 13) and $E°(W_2O_5/WO_2)$ (reaction 18) using $\Delta G_f°(WO_3) = -182.60$ kcal/mol and $\Delta G_f°(WO_2) = -127.60$ kcal/mol,[21] while $\Delta G_f°(W_2O_5) = -306.9$ kcal/mol is an old value.[19] The obtained $E°(WO_3/W_2O_5) = -0.034$ V and $E°(W_2O_5/WO_2) = 0.108$ V. This is in agreement with the recent value of $E°(WO_3/WO_2) = 0.036$ V.[18]

The redox potential $E°(H_2WO_4/W_2O_5)$ can be also calculated using $\Delta G_f°(H_2WO_4) = -239.0$ kcal/mol[22] and $\Delta G_f°(W_2O_5) = -306.9$ kcal/mol (reaction 14) via the following equation

$$E° = -\frac{1}{6}\frac{\Delta G_f°(W_2O_5) + 3\Delta G_f°(H_2O) - 2\Delta G_f°(H_2WO_4)}{F} \tag{15}$$

The obtained $E°(H_2WO_4/W_2O_5) = -0.007$ V. According to Bratsch,[18] $\Delta G_f°(H_2WO_4)$ should be equal to -237.8 kcal/mol (recalculated using his values of the potentials). Using this value, $E°(H_2WO_4/W_2O_5) = 0.009$ V. Taking into account the slightly different values of $\Delta G_f°(H_2WO_4)$, we can write $E°\ (H_2WO_4/W_2O_5) = 0 \pm 0.01$ V.

The selected data for the M^{VI} and M^{V} species are given in Table 2. There, $E°(H_2W_6O_{21}^{4-}/W^{V})$ was taken equal to -0.04 V. This value has been obtained via the thermodynamic formula on the basis of the knowledge of $E°(H_2W_6O_{21}^{4-}/W(OH)_2^{2+})$ (Table 3) and $E°(W^{V}/W(OH)_2^{2+})$ estimated via a linear correlation as it will be shown further when discussing the potentials M^{V}/M^{IV}.

To evaluate the standard reduction potentials Sg^{VI}/Sg^{V}, linear correlations have been used between the known redox potentials M^{VI}/M^{V} for Cr, Mo, and W and IPs(5+/6+). The resulting values for Sg are $E°(SgO_3/Sg_2O_5) = -0.02$, $E°(H_2SgO_4/Sg_2O_5) = -0.02$, and $E°(Sg^{VI}/Sg^{V})_{aq} = -0.03$ V. The used linear correlations are, however, very loose, and the obtained reduction potentials for Sg are not reliable. That might be explained again by a different species of Cr^{VI} than those of Mo and W. In addition, the $E°(W^{VI}/W^{V})$ values are very approximate. Thus, the potentials $E°(Sg^{VI}/Sg^{V})$ should obviously be recalculated using thermodynamic equations after more exact values of potentials Sg^{VI}/Sg^{IV} and Sg^{V}/Sg^{IV} have been defined. The way to do it is shown in section III F.

TABLE 3: Standard Free Energies of Formation, $\Delta G_f°$ (in eV), Multiple Ionization Potentials, IP(4+/6+) (in eV), and Standard Reduction Potentials $E°$ (in V) for the M^{VI}/M^{IV} Couple of Group 6 Compounds

property	Cr	Mo	W	Sg
IP(4+/6+), eV[a]	160.23	123.2	115.95	106.52
$\Delta G_f°(MO_2)$[b]	−130.97[c]	−127.39	−127.60	−127.49[i]
$E°(MO_3, H^+/MO_2)$[d]	(1.3)[e]	0.53	0.036	(−0.08)[i]
$E°(H_2MO_4, H^+/MO_2)$[d]	(1.3)[e]	(0.49)	(0.06)	(−0.08)[i]
$E°(M^{VI}, H^+/M^{IV})$[d]	(1.15)[f]	(0.4)[g]	(−0.07)[h]	(−0.20)[i]

[a] Reference 14. [b] Reference 21. [c] Reference 20. [d] Reference 18. [e] For the $(Cr_2O_7^{2-}, H^+/CrO_2)$ couple. [f] For the $(Cr_2O_7^{2-}, H^+/Cr(OH)_2^{2+})$ couple. [g] For the $(H_3Mo_7O_{24}^{3-}, H^+/Mo_2O_2^{4+})$ couple. [h] For the $(H_2W_6O_{21}^{4-}, H^+/W(OH)_2^{2+})$ couple. [i] This work.

D. Reduction Reaction $M^{VI} \rightarrow M^{IV}$. CrO_2 is known with $\Delta G_f° = -130.97$ kcal/mol. A few species of Cr^{IV} in solutions as derivatives of CrO_2^{2+} can be prepared. MoO_2 is formed with $\Delta G_f°$ of -127.39 kcal/mol, but it is unstable in water solutions.[19] Soluble species of Mo^{IV} are derivatives of the MoO^{2+} ion. At lower acidities, a binuclear structure, $Mo_2O_2^{4+}$, was proposed. Halide complexes of Mo^{IV} do not appear to be stable and disproportionate to give 3+ and 5+ states.

For tungsten dioxide, $\Delta G_f°(WO_2) = -127.6$ kcal/mol. Aqueous W^{IV} is known as $W(OH)_2^{2+}$. Aqueous forms of W^{IV} are unstable and disproportionate into the 5+ and 3+ states.

The reduction potentials for the couples M^{VI}/M^{IV} (M = Mo and W) have been calculated using free energies according to the following reactions[18,19]

$$MO_3(c) + 2H^+ + 2e \Leftrightarrow MO_2(c) + H_2O \tag{16}$$

$$H_2MO_4(c) + 2H^+ + 2e \Leftrightarrow MO_2(c) + 2H_2O \tag{17}$$

These data (Table 3) are considered to be rather accurate. They indicate that the stability of the 4+ state decreases in group 6 from Cr to W.

To evaluate standard reduction potentials $E°(Sg^{VI}/Sg^{IV})$, linear correlations have been used between IP(4+/6+) and $E°(MO_3/MO_2)$, $E°(H_2MO_4/MO_2)$, and $E°(M^{IV}/M^{IV})_{aq}$ (M = Mo and W, and $Cr_2O_7^{2-}$ is used for Cr^{VI}) for each type of the species, respectively. One of those correlations is shown in Figure 2. Estimated potentials $E°(Sg^{VI}/Sg^{IV})$ are given in Table 3 showing that the reduction $Sg^{VI} \rightarrow Sg^{IV}$ is even more difficult than $W^{VI} \rightarrow W^{IV}$. Thus, the stability of the 4+ oxidation state decreases in the group in the following way: Cr > Mo > W > Sg.

Knowing $E°$ and using reactions (16 and 17), $\Delta G_f°(SgO_2) = -127.49$ kcal/mol has been obtained.

E. Reduction Reaction $M^{V} \rightarrow M^{IV}$. To determine $E°(M_2O_5/MO_2)$, the following reaction was used

$$M_2O_5(c) + 2H^+ + 2e \Leftrightarrow 2MO_2(c) + H_2O \tag{18}$$

For Cr and Mo, the values of $E°(M_2O_5/MO_2)$ have been tabulated by Bratsch[18] (Table 4), though the potential for W was missing. Latimer[19] gives $E°(W_2O_5/WO_2) = -0.043$ V, and Bard et al.[20] give it as -0.031 V. Using a more recent value of $\Delta G_f°(WO_2) = -127.60$ kcal/mol, but still an old value of $\Delta G_f°$-

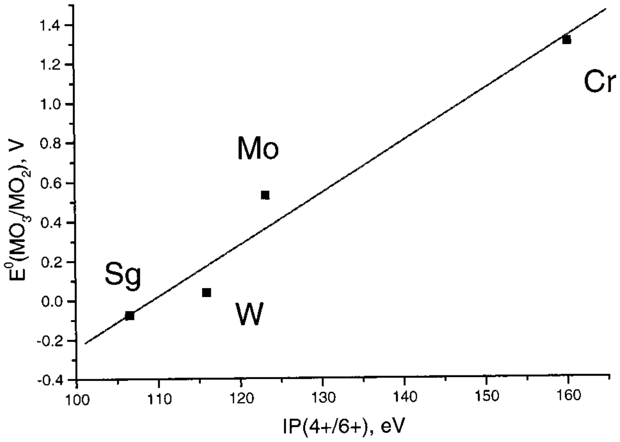

Figure 2. Correlation between IP(4+/6+) and the standard potentials $E°(Cr_2O_7^{2-}/CrO_2)$ and $E°(MO_3/MO_2)$, where M = Mo and W, (Table 3). The obtained $E°(SgO_3/SgO_2) = -0.08$ V.

TABLE 4: Standard Free Energies of Formation, $\Delta G_f°$ (in eV), Ionization Potentials, IP(4+/5+) (in V), and Standard Reduction Potentials $E°$(in V) for the M^V/M^{IV} Couple of Group 6 Compounds

property	Cr	Mo	W	Sg
IP(4+/5+)[a]	69.55	54.41	51.27	47.28
$E°(M_2O_5, H^+/MO_2)$[b]	(1.3)	(0.4)	(0.108)[c]	(−0.11)[c]
$E°(M^V, H^+/M^{IV})$[b]	(1.3)[d]	(0.2)[e]	(−0.10)[f,c]	(−0.35)[g,c]

[a] Reference 14. [b] Reference 18. [c] This work. [d] For the (H_3CrO_4, $H^+/Cr(OH)_2^{2+}$) couple. [e] For the ($Mo_2O_4^{2+}$, $H^+/Mo_2O_2^{4+}$) couple. [f] For the (W^V, $H^+/W(OH)_2^{2+}$) couple. [g] For the (Sg^V, $H^+/Sg(OH)_2^{2+}$) couple.

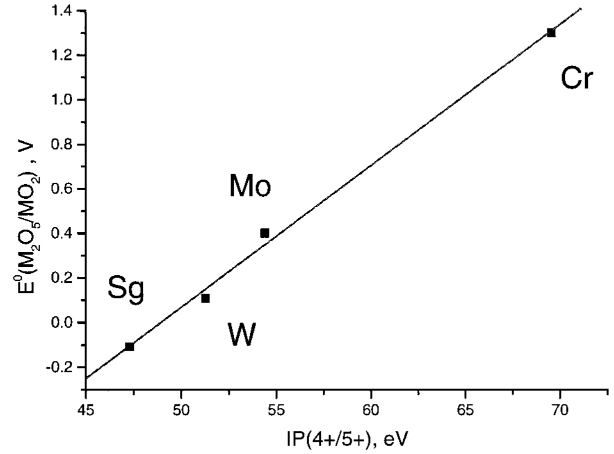

Figure 3. Correlation between IP(4+/5+) and the standard potentials $E°(M_2O_5/MO_2)$, where M = Cr, Mo, and W (Table 4). The obtained $E°(Sg_2O_5/SgO_2) = -0.11$ V.

$(W_2O_5) = -306.9$ kcal/mol, a new value of $E°(W_2O_5/WO_2) = 0.108$ V has been calculated by us. This value has been used in the correlation between IP(4+/5+) and $E°(M_2O_5/MO_2)$ for Cr, Mo, and W to obtain $E°(Sg_2O_5/SgO_2)$. As Figure 3 shows, the points fit the plot very well. The obtained $E°(Sg_2O_5/SgO_2) = -0.11$ V.

Using $\Delta G_f°(SgO_2) = -127.49$ kcal/mol and reaction 18, $\Delta G_f°(Sg_2O_5) = -316.65$ kcal/mol has been determined.

For species in solutions, the potentials M^V/M^{IV} for Cr and Mo have also been given by Bratsch[18] (Table 4). $E°[W^V/W(OH)_2^{2+}]$ has been estimated by us in a way that a linear correlation between the redox potentials M^V/M^{IV} and IPs for aqueous solutions looks similar to the one for the crystalline compounds (Figure 3). In this way, $E°[W^V/W(OH)_2^{2+}] = -0.1$ V has been obtained. Using the same plot, $E°[Sg^V/Sg(OH)_2^{2+}] = -0.35$ V has been estimated.

TABLE 5: Ionization Potentials, IP(3+/4+) (in eV), and Standard Reduction Potentials $E°$ (in V) for the M^{IV}/M^{III} Couple of Group 6 Compounds

property	Cr	Mo	W	Sg
IP(3+/4+)[a]	49.16	40.29	37.99	35.40
$E°(MO_2, H^+/M^{3+})$[b]	(1.48)	(−0.2)	(−0.9)	(−1.34)[c]
$E°(M(OH)_2^{2+}, H^+/M^{3+})$[b]	(1.8)	(0.1)[d]	(−0.5)	(−0.98)[c]

[a] Reference 14. [b] Reference 18. [c] This work. [d] For the ($Mo_2O_2^{4+}$, H^+/Mo^{3+}) couple.

Thus, the potentials Sg^V/Sg^{IV} show that the stability of the 4+ oxidation state of group 6 elements in relation to the 5+ state decreases according to Cr > Mo > W > Sg.

F. Estimates of Potentials M^{VI}/M^V Using the Thermodynamic Equation. Since the linear correlations between IP(5+/6+) and $E°(M^{VI}/M^V)$ are not satisfactory, we will now recalculate these potentials using the obtained $E°(Sg^{VI}/Sg^{IV})$ and $E°(Sg^V/Sg^{IV})$.

The thermodynamic formula gives the following expression for the potential M^{VI}/M^V

$$E°(M^{VI}/M^V) = 2\,E°(M^{VI}/M^{IV}) - E°(M^V/M^{IV}) \qquad (19)$$

Using eq 19, more accurate values of the potentials $E°(Sg^{VI}/Sg^V)$ have been obtained (Table 2). These values better fit the correlations between IP(5+/6+) and $E°(M^{VI}/M^V)$.

With the more accurate values of $E°(Sg^{VI}/Sg^V)$ we can conclude that the stability of the 5+ oxidation state in relation to the 6+ state of the group 6 elements changes in the following way: Cr > Mo > W > Sg.

G. Reduction Reaction $M^{IV} \rightarrow M^{III}$. The most important ion of Cr^{III} is $Cr(H_2O)_6^{3+}$ which is simply written as Cr^{3+}. Equilibria including this ion have been well studied. In hydrochloric acid solutions, Cr^{III} forms chloride complexes where $CrCl_2(H_2O)_4^+$ is one of the most important.

$Mo(H_2O)_6^{3+}$ is unstable and is easily oxidized by air to Mo^V (ref 20). (The 3+ state is stable with respect to its own oxidation and reduction.[19]) Under an inert atmosphere, the ion is slowly oxidized by water to Mo^{IV}. Some complexes are formed depending on the acid concentration, and in aqueous solutions of HCl > 9 M, $MoCl_6^{3-}$ is stable. The simple W^{3+} ion is unstable in solution.

For the $M^{IV} \rightarrow M^{III}$ reduction, the following reaction was used

$$MO_2(c) + 4H^+ + e \leftrightarrow M^{3+} + 2H_2O \qquad (20)$$

Estimates of the potentials for Cr, Mo, and W are given by Bratsch[18] (Table 5).

One of the correlations between IP(3+/4+) and $E°(M^{IV}/M^{III})$ is shown in Figure 4 as an example. The obtained values are $E°(SgO_2/Sg^{3+}) = -1.34$ and $E°[Sg(OH)_2^{2+}/Sg^{3+}] = -0.98$ V.

Thus, the stability of the 3+ oxidation state with respect to the 4+ state decreases in the group according to Cr > Mo > W > Sg.

H. Reduction Reaction $M^{VI} \rightarrow M^{III}$. As was already mentioned, Mo and W cannot be reduced in aqueous solutions below the 3+ state. Therefore, the reduction reaction $M^{VI} \rightarrow M^{III}$ is of high interest to prove whether Sg can be easily reduced to the 3+ state.

$E°(Cr_2O_7^{2-}/Cr^{3+})$ has been calculated from free energies.[18,19] $E°(M^{VI}/M^{3+})$ for Mo and W have been calculated by us using

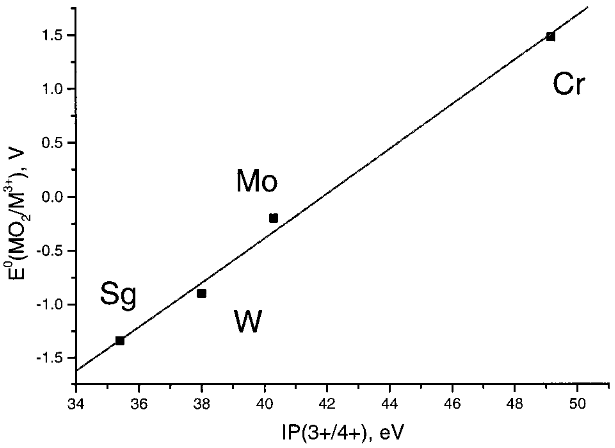

Figure 4. Correlation between IP(3+/4+) and the standard potentials $E°(MO_2/M^{3+})$, where M = Cr, Mo, and W, (Table 5). The obtained $E°(SgO_2/Sg^{3+}) = -1.34$ V.

TABLE 6: Multiple Ionization Potentials, IP(3+/6+) (in eV), and Standard Reduction Potentials $E°$ (in V) for the M^{VI}/M^{III} Couple of Group 6 Compounds

property	Cr	Mo	W	Sg
IP(3+/6+)[a]	209.39	163.49	153.94	141.92
$E°(MO_3, H^+/M^{3+})$[b]	1.36[b,c]	(0.287)[d]	(−0.276)[d]	(−0.49)[e]
$E°(H_2MO_4, H^+/M^{3+})$[b]	1.36[b,c]	(0.26)[d]	(−0.26)[d]	(−0.5)[e]
$E°(M^{VI}, H^+/M^{3+})$[b]	1.36[b,c]	(0.3)[f]	(−0.21)[g]	(−0.46)[h]

[a] Reference 14. [b] Reference 18. [c] For the $(Cr_2O_7^{2-}, H^+/Cr^{3+})$ couple. [d] Calculated by us using $E°(MO_3/MO_2)$ and $E°(MO_3/M^{3+})$. [e] This work. [f] For the $(H_3Mo_7O_{24}^{3-}, H^+/Mo^{3+})$ couple. [g] For the $(H_2W_6O_{21}^{4-}, H^+/W^{3+})$ couple. [h] Obtained in the present work via eq 21.

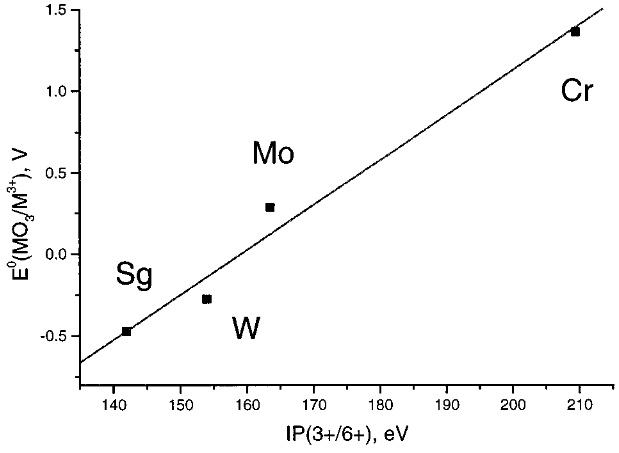

Figure 5. Correlation between IP(3+/6+) and the standard potentials $E°(Cr_2O_7^{2-}/Cr^{3+})$ and $E°(MO_3/M^{3+})$, where M = Mo and W, (Table 6). The obtained $E°(SgO_3/Sg^{3+}) = -0.48$ V.

the thermodynamic formula

$$E°(M^{VI}/M^{III}) = 1/3[2E°(M^{VI}/M^{IV}) + E°(M^{IV}/M^{III})] \quad (21)$$

The obtained values are given in Table 6. One correlation between $E°(M^{VI}/M^{3+})$ and IP(3+/6+) is shown in Figure 5. The obtained $E°(SgO_3/Sg^{3+}) = -0.48$, $E°(H_2SgO_4/Sg^{3+}) = -0.48$, and $E°(Sg^{VI}/Sg^{3+})_{aq} = -0.43$ V.

$E°(M^{VI}/M^{3+})$ can also be calculated using the thermodynamic formula (eq 21). The obtained values are $E°(SgO_3/Sg^{3+}) = -0.49$, $E°(H_2SgO_4/Sg^{3+}) = -0.5$, and $E°(Sg^{VI}/Sg^{3+})_{aq} = -0.46$ V, which are in good agreement with those obtained via the correlation. The results are summarized in Table 6.

Thus, the stability of the 3+ oxidation state in group 6 decreases according to Cr > Mo > W > Sg. This means, it is more difficult to reduce Sg^{VI} to Sg^{3+} than W^{VI} to W^{3+}; however, reduction of Sg^{VI} to Sg^{3+} should be feasible experimentally.

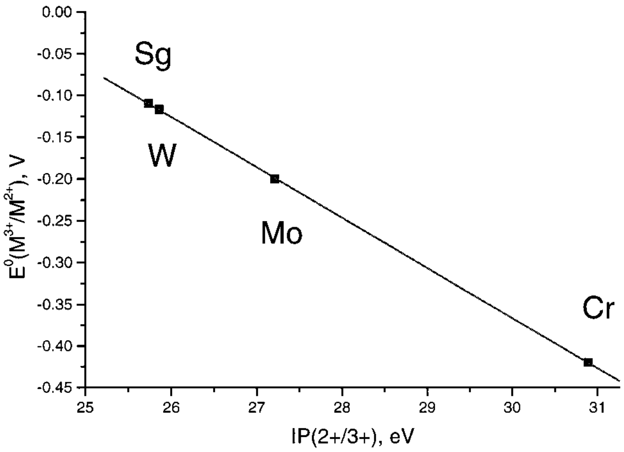

Figure 6. Correlation between IP(2+/3+) and the standard potentials $E°(M^{3+}/M^{2+})$, where M = Cr, Mo, and W for aqueous species (Table 7). The obtained $E°(Sg^{3+}/Sg^{2+}) = -0.11$ V.

TABLE 7: Ionization Potentials, IP(2+/3+) (in eV), and Standard Reduction Potentials $E°$ (in V)for the M^{III}/M^{II} Couple of Group 6 Compounds

property	Cr	Mo	W	Sg
IP(2+/3+)[a]	30.89	27.21	25.86	25.74
$E°(M^{3+}, H^+/M^{2+})$[b]	−0.42	(−0.2)	(−0.117)[c]	(−0.11)[c]

[a] Reference 14. [b] Reference 18. [c] This work.

TABLE 8: Multiple Ionization Potentials, IP(0/3+) (in eV), and Standard Reduction Potentials $E°$ (in V) for the M^{III}/M Couple of Group 6 Compounds

property	Cr	Mo	W	Sg
IP(0/3+)[a]	54.09	50.57	49.67	50.65
$E°(M^{3+}, H^+/M)$[b]	−0.74	(−0.13)	(0.1)	(0.27)[c]

[a] Reference 14. [b] Reference 18. [c] This work.

I. Reduction Reaction $M^{III} \rightarrow M^{II}$. The potential $E°(Cr^{3+}/Cr^{2+})$ has been obtained by direct cell measurements.[18,19] The red aquo ion Mo_2^{4+} can be prepared by special reactions, but it is unstable and oxidized by air to Mo^{IV} and Mo^{V}. $E°(Mo^{3+}/Mo_2^{4+})$ has been estimated.[18] No data are available for the W^{III}/W^{II} couple.

To estimate $E°(W^{3+}/W^{2+})$ and $E°(Sg^{3+}/Sg^{2+})$, a linear correlation was used between IP(2+/3+) and $E°(M^{3+}/M^{2+})$, where M = Cr, Mo, W, and Sg, (Figure 6). The obtained data are given in Table 7.

Thus, the stability of the 2+ oxidation state in relation to the 3+ state increases in the following way: Cr < Mo < W < Sg.

J. Reduction Reactions $M^{III} \rightarrow M$ and $M^{IV} \rightarrow M$. Potentials for the following reduction reaction

$$M^{3+} + 3e \Leftrightarrow M(c) \quad (22)$$

where M = Cr, Mo, and W have been calculated using thermodynamic data.[18,19] $E°(Sg^{3+}/Sg)$ can be calculated from the already estimated redox potentials using thermodynamic formulas, e.g.,

$$E°(M^{III}/M) = 1/3[6E°(M^{VI}/M) - 3E°(M^{VI}/M^{III})] \quad (23)$$

The potentials for Sg obtained in this way are given in Table 8.

In a similar way, $E°(Sg^{IV}/Sg)$ could be calculated via the following equation

$$E°(\mathrm{M^{IV}/M}) = 1/4[6E°(\mathrm{M^{VI}/M}) - 2E°(\mathrm{M^{VI}/M^{IV}})] \quad (24)$$

The results for Sg are shown in Table 9.

IV. Discussion of the Stability of the Oxidation States

Complete schemes of the redox potentials for group 6 crystalline and aqueous compounds are shown in Figures 7 and 8. These data indicate that the stability of the 6+ oxidation state increases in the group, while the relative stability of the 5+, 4+, and 3+ states decreases. In contrast to some expectations,[4] the 4+ state (in a complex form denoted as $\mathrm{Sg^{IV}}$) turned out to be even less stable than the 4+ state of W ($\mathrm{W^{IV}}$).

All of this is easy to understand by looking at the relative positions of the energy levels of the valence electrons and the ionization process. These levels obtained as a result of the DF calculations of neutral atoms[23] are shown in Figure 9.

As was shown earlier on the example of group 4 and 5 elements,[24,13] there are opposite trends in the nonrelativistic and relativistic energies of the valence orbitals with increasing Z: the nonrelativistic *n*s orbitals are destabilized while the relativistic ones are stabilized; the nonrelativistic ($n-1$)d orbitals are stabilized while the relativistic ones are destabilized. As a result, the valence 6d levels of Sg lie above the 7s level, and the first ionized electron is a $6d_{3/2}$ electron, in contrast to the 4s, 5s, and 6s electrons of Cr, Mo, and W, respectively. This results in still a larger value of the IP(0/1+) of Sg in comparison with W and the other homologues, but not as large as if it were due to the ionization of the 7s electron. The second ionized electron of Sg is 7s, therefore IP(1+/2+) for Sg is larger than IP(1+/2+) for W. For further ionization processes, the ionization potentials decrease from Cr to Sg (except for the ionization $\mathrm{Sg^{2+}} \rightarrow \mathrm{Sg^{3+}}$ from the 7s orbital), since ionization starts from the $(n-1)d_{3/2}$ orbitals which are gradually destabilized from Cr to Sg. The multiple IP(0/6+), reflecting a summary process, decreases from Cr to Sg which means that Sg reaches more easily its 6+ oxidation state than the other homologues (Figure 1). (Figure 9 demonstrates that the ionization process Sg(0 → 6+) is facilitated by close spacing of the valence levels.)

Orbital energies for the stepwise ionization process of Sg are shown in Figure 10. They have been obtained by us as a result of the single-configuration DF calculations for the relativistic electronic MCDF configurations. These energies clearly show why the 4+ state of Sg will be not stable: There is no simple stepwise ionization of the four less bound outer $6d_{3/2}$ electrons, so that the $7s^2$ electron pair stabilized by relativity is left, resulting in an increased stability of the 4+ state. After the first $6d_{3/2}$ electron has been ionized, the $6d_{3/2}$ level goes down, even below the 7s level. Thus, the next two ionized electrons of Sg are not the $6d_{3/2}$, but the 7s ones. As a result, $\mathrm{Sg^{4+}}$ has not the $7s^2$ electronic configuration, but $6d_{3/2}{}^2$. Since the $(n-1)$d electrons are steadily destabilized from Cr to Sg due to indirect relativistic effects, the ionization of the $6d_{3/2}$ electron is easier than the ionization of the $3d_{3/2}$, $4d_{3/2}$, and $5d_{3/2}$ electrons of Cr, Mo, and W, respectively (Figure 9). This means that the stability of the 4+ oxidation state decreases in the following way: Cr > Mo > W > Sg, as is shown by the correlations in Figures 2 and 3.

The same arguments are valid for the ionization process of element 105, Db. The MCDF calculations have shown that the 3+ state of Db has the same $6d^2$ electronic configuration. Therefore, the stability of the 3+ state in group 5 changes according to V > Nb > Ta > Db.

TABLE 9: Multiple Ionization Potentials, IP(0/4+) (in eV), and Standard Reduction Potentials $E°$ (in V) for the $\mathrm{M^{IV}/M}$ Couple of Group 6 Compounds

property	Cr	Mo	W	Sg
IP(0/4+)[a]	103.25	90.86	87.66	86.05
$E°(\mathrm{MO_2, H^+/M})$[b]	(−0.185)[c]	−0.152	−0.154	(−0.134)[d]
$E°(\mathrm{M(OH)_2^{2+}, H^+/M})$[b]	(−0.185)[e]	(−0.073)[f]	(−0.05)	(−0.035)[d]

[a] Reference 14. [b] Reference 18. [c] Calculated by us using $E°(\mathrm{CrO_2/Cr^{3+}})$ and $E°(\mathrm{Cr^{3+}/Cr})$. [d] This work. [e] Calculated by us using $E°[\mathrm{Cr(OH)_2^{2+}/Cr^{3+}}]$ and $E°(\mathrm{Cr^{3+}/Cr})$. [f] For the ($\mathrm{Mo_2O_2^{4+}, H^+/Mo}$) couple.

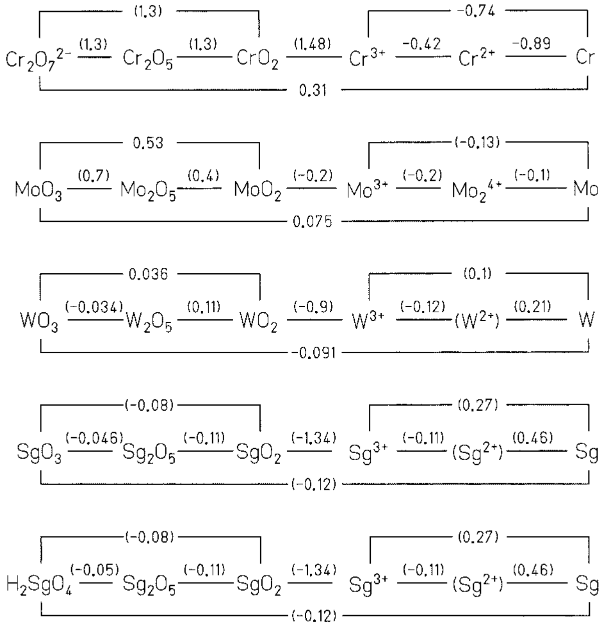

Figure 7. Standard reduction potentials for group 6 crystalline and aqueous phase compounds.

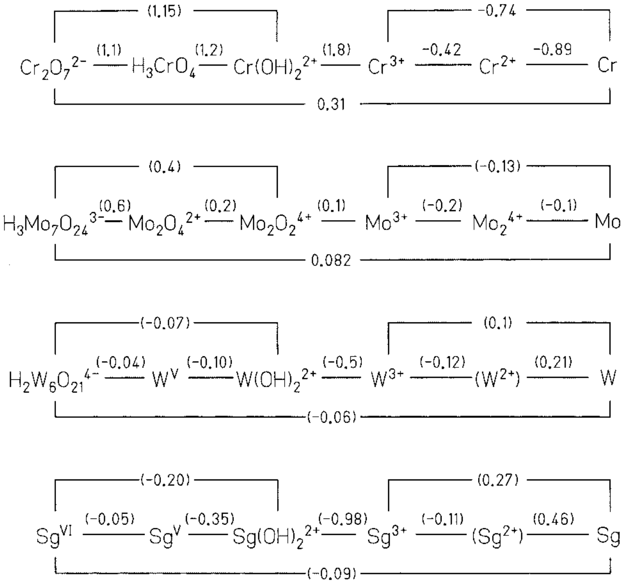

Figure 8. Standard reduction potentials for group 6 aqueous phase compounds.

Finally, it is interesting to compare the relative stability of the 4+ and 3+ oxidation states in group 6. From the data of Table 10, one can see that it is easier to reduce $\mathrm{Cr^{VI}}$ to the 3+ state than to the 4+ state, while it is easier to reduce $\mathrm{Mo^{VI}}$ to the 4+ state than to the 3+ state. Thus, the relative stability of the 4+ state with respect to the 3+ state increases in group 6. Therefore, it is easier to reduce $\mathrm{Sg^{VI}}$ to the $\mathrm{Sg^{IV}}$ state than to the $\mathrm{Sg^{3+}}$ state.

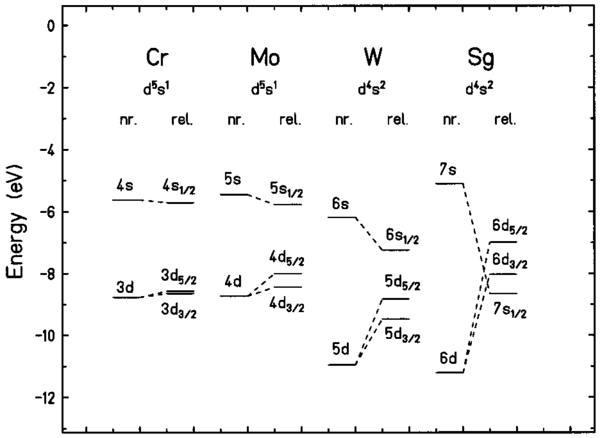

Figure 9. Relativistic (rel.) and nonrelativistic (nr.) DF energies[23] of the valence electrons of group 6 elements.

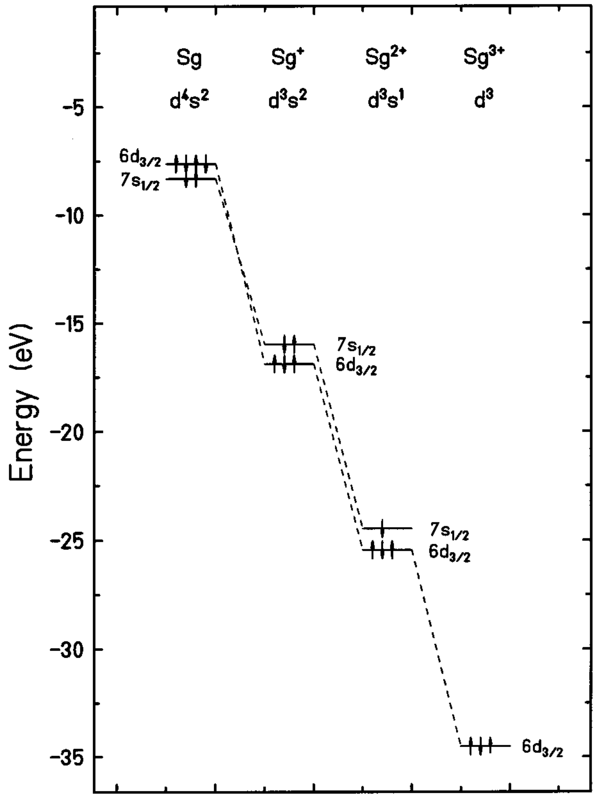

Figure 10. Relativistic MCDF orbital energies of the neutral through third ionized states of Sg.

TABLE 10: Standard Reduction Potentials $E°(M^{VI}/M^{IV})$ and $E°(M^{VI}/M^{III})$ (in V) for Group 6 Compounds

potential	Cr	Mo	W	Sg
$E°(M^{VI}, H^+/M^{IV})^a$	1.30	0.53	0.036	−0.08
$E°(M^{VI}, H^+/M^{III})^a$	1.36	(0.287)[b]	(−0.276)[b]	(−0.49)[c]

[a] Reference 18. [b] Calculated by us using $E°(MO_3/MO_2)$ and $E°(MO_2/M^{3+})$. [c] This work.

V. Conclusions

The present estimates of reduction potentials for group 6 elements including Sg have shown that the stability of the maximum oxidation state increases within group 6, though this increase with respect to the 5+ oxidation state is very small. The stability of the 5+, 4+, and 3+ oxidation states decreases within group 6, so that in contrast to expectations, the 4+ oxidation state of Sg in a complex form will not be preferentially stabilized. This is well explained by the known fact that influence of relativistic effects on the valence electron shells weakens with increasing atomic/ionic charge. Therefore, relativistic effects for the Sg^{4+} state are not strong enough to stabilize the $7s^2$ electronic pair, therefore the lowest electronic configuration of the tetrapositive seaborgium is $6d^2$, exactly as those of the lighter homologues in the group, Cr, Mo, and W. Thus, no deviation from the Mendeleev-type periodicity, or periodicity based on the electronic configurations, is observed for such a property as an oxidation state in group 6 in going over to the transactinide element, Sg.

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